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ABSTRACT

In the problem of evaluating two and three-center integrals which give rise to infinite series, the one and two-electron integrals (which are three and six-dimensional integrals) are reduced to infinite series of one and two-dimensional integrals respectively. Convergence rates and asymptotic behavior for large order terms of the series are derived.

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1. Introduction

The expression of the solutions of Schrödinger's equation for the electronic configuration of a molecule as a linear combination of given atomic orbital functions transforms Schrödinger's equation into a matrix equation. The solution of this matrix equation involves the evaluation of certain three and six-dimensional integrals referred to as one and two-electron integrals, respectively. The domains of integration of the integrals are all of Euclidean three and six space. Some of the general techniques for evaluating these integrals involve integrating over certain of the variables, transforming the integrals into series of one and two-dimensional integrals.

The exact form of these series depends upon the choice of coordinate system in Euclidean three space. Once the choice of coordinate system has been made and the integrations carried out, the integrals fall into two categories: those involving infinite series and those involving finite series.

Two methods are commonly used in the evaluation of these integrals, each based upon a particular choice of coordinate system in Euclidean three space. One method involves carrying out the integrations using prolate spheroidal coordinates. The evaluation of the monocenter and two-center integrals using this method has been carried out by some earlier workers [3,4,5,6,7].

The other method involves carrying out the integrations, using spherical coordinates. The evaluation of the two center integrals involving a finite series, (the one electron, two electron monocenter, and two center hybrid and coulomb integrals), using this method has been carried out by Barnett and Coulson [1].

The advantages of the first method over the second in the evaluation of these integrals are: (1) more of the two center integrals involve only a finite series, and (2) the infinite series obtained appear to converge rapidly. The advantages of the second method over the first are:(1) the special functions are relatively easy to compute, and (2) the second method can more readily be extended to the evaluation of three and four center integrals (arising from problems in the molecular structure of molecules with three and four atoms).

In this paper we shall be concerned with the evaluation of some of the two and three center integrals of molecular structure. Because we wish to evaluate all of the three center integrals, we shall use the method involving spherical coordinates. Using this method we shall evaluate those two and three center integrals which give rise to infinite series, namely:

(1.1) $$\int_1 \psi_A^{(1)}(1) r_{C1}^{-1} \psi_B^{(2)}(1)\, dv_1$$ (potential energy integrals)

(1.2) $$\int_2\int_1 \psi_A^{(1)}(1)\psi_B^{(2)}(1) r_{12}^{-1} \psi_A^{(3)}(2)\psi_B^{(4)}(2) dv_1 dv_2$$

(two center exchange integrals)

(1.3) $$\int_2\int_1 \psi_A^{(1)}(1)\psi_B^{(2)}(1) r_{12}^{-1} \psi_A^{(3)}(2)\psi_C^{(4)}(2) dv_1 dv_2$$

(three center hydrid exchange integrals)

(1.4) $$\int_2\int_1 \psi_B^{(1)}(1)\psi_B^{(2)}(1) r_{12}^{-1} \psi_A^{(3)}(2)\psi_C^{(4)}(2) dv_1 dv_2$$

(three center coulomb exchange integrals)

$\rho_B = \overline{AB}$ $\qquad \rho_C = \overline{AC}$

$< CAB = \alpha$

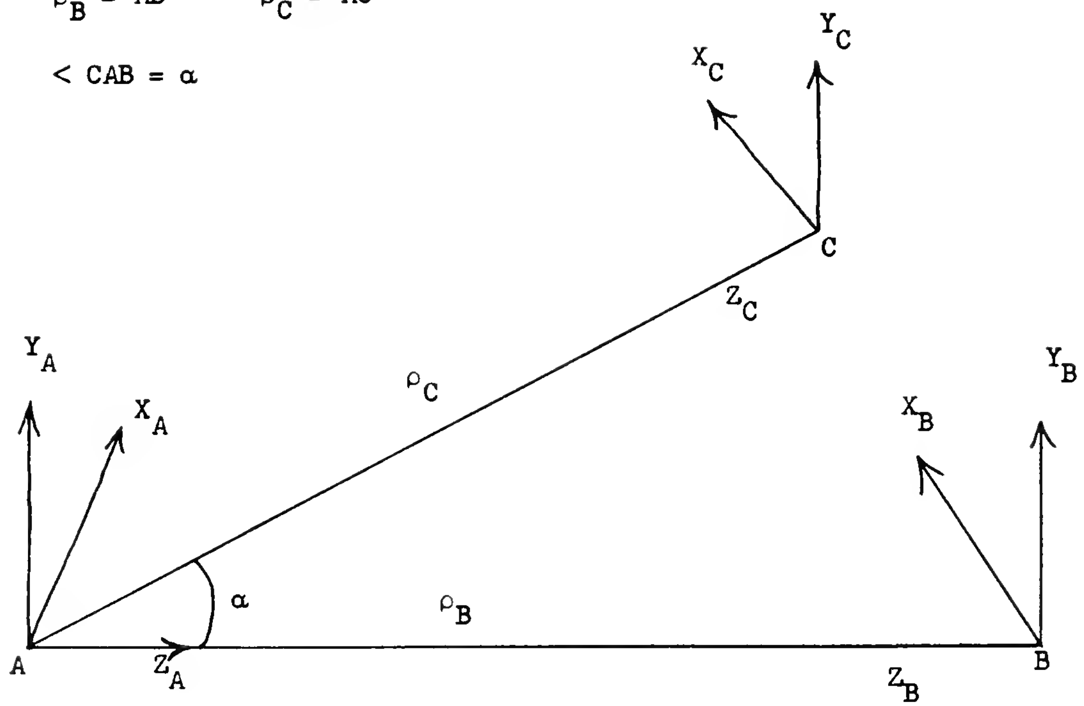


FIGURE 1

In order to define precisely what these integrals are, we may consider the case of a general triatomic molecule in three dimensional space (see Figure 1), where A, B, C are three arbitrary noncolinear points in space (the locations of the three nuclei of the atoms of the molecule). We define three rectangular coordinate systems (x_μ, y_μ, z_μ) μ = A, B, or C with A, B, C as origins as follows. y_A, y_B, y_C have the same direction and are perpendicular to the plane determined by A, B, C. z_A is taken along AB directed toward B and z_B, z_C are taken along AB, AC respectively, directed toward A. x_A, x_B, x_C are chosen so that (x_A, y_A, z_A) is a right-handed coordinate system and (x_μ, y_μ, z_μ) μ = B, C are left-handed coordinate systems. In terms of these rectangular coordinate systems we may define spherical coordinate systems $(r_\mu, \theta_\mu, \phi_\mu)$ with origins at μ = A, B, C respectively.

With these definitions, then, we may define the integrals (1.1) - (1.4). The $\psi^{(i)}(\delta)$; $i = 1,2,3,4$; $\mu = A,B,C$; $\delta = 1,2$ are among the Slater functions given in Appendix (1). Here we restrict ourselves to Slater functions involving major quantum numbers $n = 1$ or 2. $(r_{\mu\delta}, \theta_{\mu\delta}, \phi_{\mu\delta})$ $\mu = A, B, C$; $\delta = 1,2$ are the spherical coordinates of electron δ with origin μ. r_{12} is the distance of electron 2 from electron 1 and an expansion for r_{12}^{-1} is given in Appendix (1). dv_δ, $\delta = 1,2$ are volume elements.

2. Method of evaluation of the integrals

The method of evaluating the integrals used in this paper is usually referred to as the Bessel Function Method [1], and consists essentially in the expansion of functions with arguments $(r_\mu, \theta_\mu, \phi_\mu)$ $\mu = B$ or C in terms of functions with arguments (r_A, θ_A, ϕ_A). The expansions used for this purpose are given in Appendix (2), and their derivation is straightforward.

The use of the Bessel Function Method in evaluating integrals (1.1)-(1.4) gives rise to an infinite series of single integrals in the case of integral (1.1) and infinite series of double integrals in the case of integrals (1.2)-(1.4). It is the purpose of this paper to establish the rates of convergence of these series and to obtain the asymptotic behavior of the general terms of large order in these series.

The actual techniques for reducing the three and six dimensional integrals to an infinite series of one and two dimensional integrals respectively and the analysis of the asymptotic behavior and the convergence rates of the series are practically identical for the four cases, but are somewhat tedious and difficult to explain without using one of the four cases as an example. Therefore the general techniques and methods will be explained, integral (1.1) as an example, and the ex-

planation will not be repeated in the other three cases unless a variation in the techniques is encountered.

3. Potential energy integrals

These are of the form:

$$(3.1)\quad \int_1 \psi_A^{(1)}(1) r_{C1}^{-1} \psi_B^{(2)}(1) dv_1$$

$$= C_1 C_2 \sum_{i_1=0}^{\infty} \sum_{j=0}^{i_1} E'_{i_1 j} P_{i_1}^{j}(\cos\alpha) \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} r_{A1}^{n_1+1} e^{-k_1 r_{A1}}$$

$$\times\, r_{B1}^{n_2-1} e^{-k_2 r_{B1}} \left(\rho_{C<}^{i_1} \Big/ \rho_{C>}^{i_1+1} \right) P_{i_1}^{j}(\cos\theta_{A1})$$

$$\times\, P_{\ell_1}^{|m_1|}(\cos\theta_{A1})\, P_{\ell_2}^{|m_2|}(\cos\theta_{B1}) \sin\theta_{A1}$$

$$\times\, \Phi_{m_1}(\phi_{A1})\, \Phi_{m_2}(\phi_{A1}) \cos j\,\phi_{A1}\, d\phi_{A1} d\theta_{A1} dr_{A1}\,.$$

Starting with the ϕ_{A1} variable, we note by the formulas for expanding products of sines and cosines that the integral must vanish unless the expansion of $\Phi_{m_1}(\phi_{A1})\Phi_{m_2}(\phi_{A1})$ in terms of a linear combination of sines and cosines contains a term: $\cos M\phi_{A1}$, $M = |m_1 \pm m_2|$. If this is the case, integration over the ϕ_{A1} variable transforms the series into a linear combination of at most two infinite series of integrals of the type:

$$(3.2)\quad \sum_{i_1=M}^{\infty} E'_{i_1 M} P_{i_1}^{M}(\cos\alpha) \int_0^{\infty}\int_0^{\pi} r_{A1}^{n_1+1} e^{-k_1 r_{A1}} r_{B1}^{n_2-1} e^{-k_2 r_{B1}} \left(\rho_{C<}^{i_1} / \rho_{C>}^{i_1+1} \right)$$

$$P_{i_1}^{M}(\cos\theta_{A1}) P_{\ell_1}^{|m_1|}(\cos\theta_{A1}) P_{\ell_2}^{|m_2|}(\cos\theta_{B1}) \sin\theta_{A1}\, d\theta_{A1} dr_{A1}.$$

Passing to the θ_{A1}, θ_{B1} variables, we first expand

$$r_{B1}^{\ell_2} P_{\ell_2}^{|m_2|}(\cos \theta_{B1})$$

in terms of r_{A1}, ρ_B, and $P_{\ell_3}^{|m_3|}(\cos \theta_{A1})$ where $0 \le |m_3| \le \ell_3 \le 1$ by means of the expansions given in Appendix (2). We then expand $r_{B1}^{n_2-\ell_2-1} e^{-k_2 r_{B1}}$ in terms of r_{A1}, θ_{A1}, ρ_B, also by means of the expansions given in the same appendix. The result is a linear combination of at most two infinite series of integrals of the form:

$$(3.3) \qquad \sum_{i_1=M}^{\infty} \sum_{i_2=0}^{\infty} E'_{i_1 M}(2i_2+1) P_{i_1}^{M}(\cos \alpha) \int_0^{\infty} \int_0^{\pi} \times r_{A1}^{\tau+1/2} e^{-k_1 r_{A1}} f_{i_2}(k_2, r_{A1}, \rho_B) \left(\rho_{C<}^{i_1} / \rho_{C>}^{i_1+1} \right) \times P_{i_2}(\cos \theta_{A1}) P_{i_1}^{M}(\cos \theta_{A1}) P_{\ell_1}^{|m_1|}(\cos \theta_{A1}) P_{\ell_3}^{|m_3|}(\cos \theta_{A1}) \sin \theta_{A1}\, d\theta_{A1}\, dr_{A1}$$

where $0 \le |m_3| \le \ell_3 \le 1$, $\tau = n_1 + 1$ or $n_1 + 2$ and f_{i_2} = either p_{i_2} or q_{i_2} defined in Appendix (2). We then expand

$$(3.4) \qquad P_{i_1}^{M}(\cos \alpha) = \sin^{-M} \alpha (\sin^M \alpha)\, P_{i_1}^{M}(\cos \alpha)$$

$$= \sin^{-M} \alpha \sum_{i=0}^{M} G_{i_1 M0i}\, P_{i_1-M+2i}(\cos \alpha) \quad (\sin \alpha \neq 0).$$

This expansion is given in Appendix (3). We now note that the only possibilities for M are 0, 1 or 2. Considering each case separately, we can expand

$$P_{\ell_1}^{|m_1|}(\cos\theta_{A1})P_{\ell_3}^{|m_3|}(\cos\theta_{A1})P_{i_1}^{M}(\cos\theta_{A1})$$

as a linear combination of Legendre polynomials $P_{i_1+\tau_1}(\cos\theta_{A1})$ with the G's as coefficients, as defined in Appendix (3). We now may integrate over the θ_{A1} variable using the orthogonality properties of the Legendre polynomials. The general result in each of the three cases M = 0,1, or 2 is that

$$(3.5)\qquad E'_{i_1M}(2i_2+1)P_{i_1}^{M}(\cos\alpha)\int_0^{\pi} P_{i_2}(\cos\theta_{A1})P_{i_1}^{M}(\cos\theta_{A1}) \times P_{\ell_1}^{|m_1|}(\cos\theta_{A1})P_{\ell_3}^{|m_3|}(\cos\theta_{A1})\sin\theta_{A1}\,d\theta_{A1}$$

$$= \sin^{-M}\alpha\sum_{\tau_1\tau_5} A_{i_2\tau_1\tau_5}P_{i_2+\tau_1}(\cos\alpha)$$

where τ_1,τ_5 take on only a finite number of integer values. This number is independent of i_2, and the $A_{i_2\tau_1\tau_5}$ are rational functions of i_2, with the degree of the numerator equalling the degree of the denominator. By the orthogonality conditions on the Legendre polynomials, i_1, i_2 are now not independent so the $A_{i_2\tau_1\tau_5}$ may be regarded as a function only of i_2. By the general result stated above

$$\lim_{i_2\to\infty} A_{i_2\tau_1\tau_5} = \text{constant} \neq \pm\infty,\ 0$$

so that the coefficients $A_{i_2\tau_1\tau_5}$ do not affect the convergence of the infinite series of integrals.

After integration over θ_{A1} the infinite series becomes a finite linear combination of infinite series of integrals of the type:

$$(3.6)\qquad \sum_{i}^{\infty} P_{i+\tau_1}(\cos\alpha)\int_0^{\infty} r_{Al}^{\tau_2+\frac{1}{2}} e^{-k_1 r_{Al}} f_{i+\tau_3}(k_2, r_{Al}, \rho_B)\left(\rho_{C<}^{i} / \rho_{C>}^{i+1}\right) dr_{Al}$$

where the τ's are small fixed integers, and where the subscript on i is dropped. Since $f_{i+\tau_3} = p_{i+\tau_3}$ or $q_{i+\tau_3}$ as defined in Appendix (2), and $q_{i+\tau_3} = k_2^{-1} p_{i+\tau_3}$ plus (higher order terms in i),(see Appendix (2))we may take $f_{i+\tau_3} = p_{i+\tau_3}$. Writing $p_{i+\tau_3}$ as a linear combination of the functions $\gamma_{i+\tau_4}$ $\tau_4 = \tau_3 \pm 1$, we can expand (3.6) as a linear combination of at most two series of the following type:

$$(3.7)\qquad \sum_{i}^{\infty} P_{i+\tau_1}(\cos\alpha)\frac{1}{(2i+2\tau_3+1)} S_i$$

$$= \sum_{i}^{\infty} P_{i+\tau_1}(\cos\alpha)\,\frac{1}{(2i+2\tau_3+1)}\int_0^{\infty} x^{\tau_2+\frac{3}{2}} e^{-k_1 x}\gamma_{i+\tau_4}(k_2, x, \rho_B)$$

$$\times\left(\rho_{C<}^{i} / \rho_{C>}^{i+1}\right) dx \qquad \text{where } x = r_{Al}.$$

We will now proceed to obtain the rate of convergence of the series(3.7) and the asymptotic behavior of the terms of this series for large i.

The general procedure is to split the region of integration into subregions where the integrand is analytic and to consider each term of the series as a sum of integrals over each subregion. Then each of the summands is analyzed separately and in this way the overall behavior of the series is obtained. Each summand is analyzed by first noting that the integrands are non-negative. Then if the integrands are replaced by non-negative functions which are never less than the integrand and the integration carried out, a majorant series for the original series will be obtained. Similarly, by using functions which are never greater than the integrand, a minorant series for the original series will be obtained. If the majorant and minorant series have the same

asymptotic behavior and the same rate of convergence, we may then conclude that these are the asymptotic behavior and convergence rate of the original series. The functions used to replace the integrand, together with other inequalities used are derived in Appendix (4). To carry out this procedure we must consider three cases $\rho_C < \rho_B$, $\rho_C > \rho_B$, and $\rho_C = \rho_B$.

Case 1, $\rho_C < \rho_B$:

If we ignore the coefficient to the left of the integral sign for the moment, S_i can be written as a sum of three integrals:

$$S_i = S_i^1 + S_i^2 + S_i^3$$

where

$$S_i^1 = \rho_C^{-i-1} \int_0^{\rho_C} x^{\tau_2 + \frac{3}{2} + i} e^{-k_1 x} \gamma_{i+\tau_4}(k_2, x, \rho_B)\, dx \tag{3.8}$$

$$S_i^2 = \rho_C^{i} \int_{\rho_C}^{\rho_B} x^{\tau_2 + \frac{1}{2} - i} e^{-k_1 x} \gamma_{i+\tau_4}(k_2, x, \rho_B)\, dx \tag{3.9}$$

$$S_i^3 = \rho_C^{i} \int_{\rho_B}^{\infty} x^{\tau_2 + \frac{1}{2} - i} e^{-k_1 x} \gamma_{i+\tau_4}(k_2, x, \rho_B)\, dx. \tag{3.10}$$

We may now use the inequalities of Appendix (4) to deduce the following inequalities:

$$S_i^1 \geq \frac{e^{-k_2\rho_B} e^{-(k_1+k_2)\rho_C} \rho_B^{-\tau_4 - \frac{1}{2}} \rho_C^{2+\tau_2+\tau_4}}{(2i+\tau_2+\tau_4+3)(2i+2\tau_4+1)} \left(\frac{\rho_C}{\rho_B}\right)^i \tag{3.11}$$

$$(3.12)\qquad S_i^1 \le \frac{e^{(k_2-k_1)_+\rho_C}\ \rho_B^{-\tau_4-\frac{1}{2}}\ \rho_C^{2+\tau_2+\tau_4}}{(2i+\tau_2+\tau_4+3)(2i+2\tau_4+1)}\ \left(\frac{\rho_C}{\rho_B}\right)^i$$

$$(3.13)\qquad S_i^2 \ge \frac{e^{-k_2\rho_B}\ \rho_B^{-\tau_4-\frac{1}{2}}}{(2i+2\tau_4+1)}\ \left(\frac{\rho_C}{\rho_B}\right)^i \int_{\rho_C}^{\rho_B} x^{\tau_2+\tau_4+1}\, e^{-(k_1+k_2)x}\, dx$$

$$(3.14)\qquad S_i^2 \le \frac{\rho_B^{-\tau_4-\frac{1}{2}}}{(2i+2\tau_4+1)}\ \left(\frac{\rho_C}{\rho_B}\right)^i \int_{\rho_C}^{\rho_B} x^{\tau_2+\tau_4+1}\, e^{(k_2-k_1)x}\, dx$$

$$(3.15)\qquad S_i^3 \le \frac{e^{(k_2-k_1)\rho_B}\ \rho_B^{\tau_2+\frac{3}{2}}}{(2i+\tau_4-\tau_2-1)(2i+2\tau_4+1)}\ \left(\frac{\rho_C}{\rho_B}\right)^i$$

Case 2, $\rho_B < \rho_C$:

If we again ignore the coefficient to the left of the integral S_i can again be written as a sum of three integrals:

$$S_i = S_i^1 + S_i^2 + S_i^3$$

where now

$$(3.16)\qquad S_i^1 = \rho_C^{-i-1} \int_0^{\rho_B} x^{\tau_2+i+\frac{3}{2}}\, e^{-k_1x}\, \gamma_{i+\tau_4}(k_2,x,\rho_B)\, dx$$

$$(3.17)\qquad S_i^2 = \rho_C^{-i-1} \int_{\rho_B}^{\rho_C} x^{\tau_2+i+\frac{3}{2}}\, e^{-k_1x}\, \gamma_{i+\tau_4}(k_2,x,\rho_B)\, dx$$

$$(3.18)\qquad S_i^3 = \rho_C^{i} \int_{\rho_C}^{\infty} x^{\tau_2+\frac{1}{2}-1}\, e^{-k_1x}\, \gamma_{i+\tau_4}(k_2,x,\rho_B)\, dx.$$

The following inequalities may readily be deduced from Appendix (4).

$$(3.19) \qquad S_i^1 \geq \frac{e^{-(k_1+2k_2)\rho_B}\,\rho_B^{\tau_2+\frac{5}{2}}\,\rho_C^{-1}}{(2i+2\tau_4+1)(2i+\tau_4+\tau_2+3)} \left(\frac{\rho_B}{\rho_C}\right)^i$$

$$(3.20) \qquad S_i^1 \leq \frac{e^{(k_2-k_1)_+\rho_B}\,\rho_B^{\tau_2+\frac{5}{2}}\,\rho_C^{-1}}{(2i+2\tau_4+1)(2i+\tau_4+\tau_2+3)} \left(\frac{\rho_B}{\rho_C}\right)^i$$

$$(3.21) \qquad S_i^2 \geq \frac{e^{-k_2\rho_B}\,\rho_B^{\tau_4+\frac{1}{2}}\,\rho_C^{-1}}{(2i+2\tau_4+1)} \left(\frac{\rho_B}{\rho_C}\right)^i \int_{\rho_B}^{\rho_C} x^{\tau_2-\tau_4+1}\, e^{-(k_1+k_2)x}\, dx$$

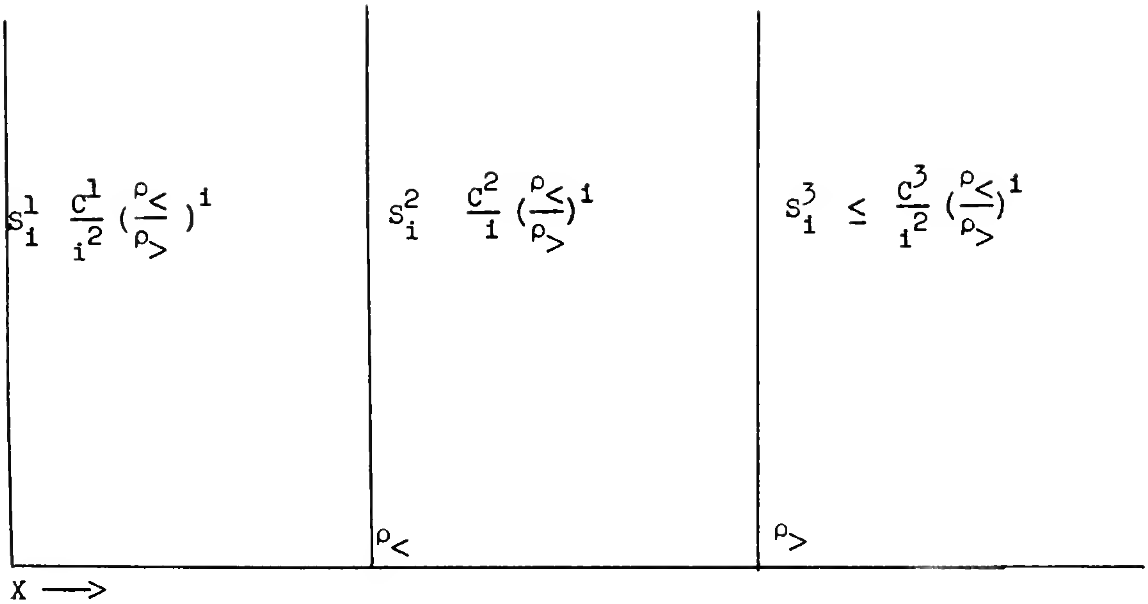
$$(3.22) \qquad S_i^2 \leq \frac{e^{k_2\rho_B}\,\rho_B^{\tau_4+\frac{1}{2}}\,\rho_C^{-1}}{(2i+2\tau_4+1)} \left(\frac{\rho_B}{\rho_C}\right)^i \int_{\rho_B}^{\rho_C} x^{\tau_2-\tau_4+1}\, e^{-k_1x}\, dx$$

$$(3.23) \qquad S_i^3 \leq \frac{e^{k_2\rho_B}\, e^{-k_1\rho_C}\,\rho_B^{\tau_4+\frac{1}{2}}\,\rho_C^{\tau_2-\tau_4+1}}{(2i+2\tau_4+1)(2i+\tau_4-\tau_2-1)} \left(\frac{\rho_B}{\rho_C}\right)^i .$$

Figure 2 summarizes the asymptotic behavior of the S_i^j, $j = 1,2,3$ in both the preceding cases deducible from the above inequalities. Returning to the original series (3.7), and now taking into account the coefficients heretofore neglected, we see that the series converge absolutely as $\frac{C}{i^{5/2}} \left(\frac{\rho_<}{\rho_>}\right)^i$ for large i. Though we only obtained a majorant series for S_i^3, this is sufficient for us to determine the asymptotic behavior of the series (3.7).

Case 3, $\rho_B = \rho_C$:

Here $S_i^2 = 0$ and $S_i = S_i^1 + S_i^3$, where S_i^1, S_i^3 can easily be seen to behave asymptotically as C^1/i^2, C^3/i^2 respectively. The absolute asymptotic behavior of the series (3.7) in this case is $\frac{C}{i^{7/2}}$ for large i.



$\rho_< = \min(\rho_B, \rho_C)$ $\qquad$ $\rho_> = \max(\rho_B, \rho_C)$

C^1, C^2, C^3 are fixed constants.

FIGURE 2

4. Two center exchange integrals

These are of the form:

$$(4.1) \qquad \int_2\int_1 \psi_A^{(1)}(1)\psi_B^{(2)}(1)r_{12}^{-1}\psi_A^{(3)}(2)\psi_B^{(4)}(2)\, dv_1 dv_2$$

$$= C_1C_2C_3C_4 \sum_{\ell=0}^{\infty}\sum_{m=0}^{\ell} D_{\ell m} \int_0^{\infty}\int_0^{\infty}\int_0^{\pi}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}$$

$$\times\, r_{A1}^{n_1+1}\, e^{-k_1 r_{A1}}\, r_{B1}^{n_2-1}\, e^{-k_2 r_{B1}} (r_{A<}^{\ell} / r_{A>}^{\ell+1}) r_{A2}^{n_3+1}\, e^{-k_3 r_{A2}}$$

$$\times\, r_{B2}^{n_4-1}\, e^{-k_4 r_{B2}}\, P_{\ell_1}^{|m_1|}(\cos\theta_{A1}) P_{\ell_2}^{|m_2|}(\cos\theta_{B1}) P_{\ell}^{m}(\cos\theta_{A1})$$

$$\times\, P_{\ell}^{m}(\cos\theta_{A2}) P_{\ell_3}^{|m_3|}(\cos\theta_{A2}) P_{\ell_4}^{|m_4|}(\cos\theta_{B2}) \sin\theta_{A1} \sin\theta_{A2}$$

$$\times\, \Phi_{m_1}(\phi_{A1})\, \Phi_{m_2}(\phi_{B1}) \cos m(\phi_{A1}-\phi_{A2})\, \Phi_{m_3}(\phi_{A2})\, \Phi_{m_4}(\phi_{B2})\, d\phi_{A1} d\phi_{A2} d\theta_{A1} d\theta_{A2}\, dr_{A1} dr_{A2} \; .$$

Beginning with the ϕ_{A1}, ϕ_{A2} variables we first expand $\Phi_{m_1}\,\Phi_{m_2}$ and $\Phi_{m_3}\,\Phi_{m_4}$ each as a linear combination of sines and cosines. The integral will vanish unless at least one sine or cosine function in the expansion of $\Phi_{m_1}\,\Phi_{m_2}$ is the same as a sine or cosine function in the expansion of $\Phi_{m_3}\,\Phi_{m_4}$. In this latter case, integration over ϕ_{A1}, ϕ_{A2} transforms (4.1) into a linear combination of at most two series of the type:

$$(4.2)\quad \sum_{\ell=M}^{\infty} D_{\ell M} \int_0^{\infty}\int_0^{\infty}\int_0^{\pi}\int_0^{\pi} r_{A1}^{n_1+1}\, e^{-k_1 r_{A1}}\, r_{B1}^{n_2-1}\, e^{-k_2 r_{B1}}$$

$$\times \left(r_{A<}^{\ell} \,/\, r_{A>}^{\ell+1}\right) r_{A2}^{n_3+1}\, e^{-k_3 r_{A2}}\, r_{B2}^{n_4-1}\, e^{-k_4 r_{B2}}$$

$$\times\; P_{\ell_1}^{|m_1|}(\cos\theta_{A1}) P_{\ell_2}^{|m_2|}(\cos\theta_{B1}) P^{M}(\cos\theta_{A1}) P_{\ell}^{M}(\cos\theta_{A2})$$

$$\times\; P_{\ell_3}^{|m_3|}(\cos\theta_{A2}) P_{\ell_4}^{|m_4|}(\cos\theta_{B2}) \sin\theta_{A1}\,\sin\theta_{A2}$$

$$\times\; d\theta_{A1}\, d\theta_{A2}\, dr_{A1}\, dr_{A2}.$$

Passing to the variables θ_{A1}, θ_{A2} we expand $r_{B1}^{\ell_2}\, P_{\ell_2}^{|m_2|}(\cos\theta_{B1})$ and $r_{B1}^{\ell_4}\, P_{\ell_4}^{|m_4|}(\cos\theta_{B2})$ in terms of r_{A1}, ρ_B, $P_{\ell_5}^{|m_5|}(\cos\theta_{A1})$ $0 \le |m_5| \le \ell_5 \le 1$ and r_{A2}, ρ_B, $P_{\ell_6}^{|m_6|}(\cos\theta_{A2})$ $0 \le |m_6| \le \ell_6 \le 1$, respectively, by the formulas of Appendix (2). Next we expand

$$r_{B1}^{n_2-\ell_2-1}\quad e^{-k_2 r_{B1}}$$

and

$$r_{B2}^{n_4-\ell_4-1}\quad e^{-k_4 r_{B2}}$$

in terms of r_{A1}, $P_{i}(\cos\theta_{A1})$, ρ_B, and r_{A2}, $P_{i_2}(\cos\theta_{A2})$, ρ_B, respectively. (See same appendix) The result of these expansions transforms (4.2) into a linear combination of at most four series of the form:

$$(4.3)\qquad \sum_{\ell=M}^{\infty}\sum_{i_1=0}^{\infty}\sum_{i_2=0}^{\infty} D_{\ell M}(2i_1+1)(2i_2+1)\int_0^{\infty}\int_0^{\infty}\int_0^{\pi}\int_0^{\pi}$$

$$\times\, r_{A1}^{\tau_1+\frac{1}{2}}\, e^{-k_1 r_{A1}} f_{i_1}(k_2, r_{A1}, \rho_B)(r_{A<}^{\ell} / r_{A>}^{\ell+1})$$

$$\times\, r_{A2}^{\tau_2+\frac{1}{2}}\, e^{-k_3 r_{A2}} f_{i_2}(k_4, r_{A2}, \rho_B) P_{i_1}(\cos\theta_{A1}) P_{\ell_1}^{|m_1|}(\cos\theta_{A1})$$

$$\times\, P_{\ell_5}^{|m_5|}(\cos\theta_{A1}) P_{\ell}^{M}(\cos\theta_{A1}) P_{\ell}^{M}(\cos\theta_{A2}) P_{\ell_3}^{|m_3|}(\cos\theta_{A2})$$

$$\times\, P_{\ell_6}^{|m_6|}(\cos\theta_{A})\; P_{i_2}(\cos\theta_{A2}) \sin\theta_{A1} \sin\theta_{A2}\, d\theta_{A1}\, d\theta_{A2}\, dr_{A1}\, dr_{A2}$$

where τ_1, τ_2 = 1,2, or 3, and f_i = either p_i or q_i defined in Appendix (2).

Now M may take on only one of three possible values: 0, 1, or 2. Considering each case separately we may expand $P_{\ell}^{M}(\cos\theta_{A1}) P_{\ell_1}^{|m_1|}(\cos\theta_{A1}) \times P_{\ell_5}^{|m_5|}(\cos\theta_{A1})$ and $P_{\ell}^{M}(\cos\theta_{A2}) P_{\ell_3}^{|m_3|}(\cos\theta_{A2}) P_{\ell_6}^{|m_6|}(\cos\theta_{A2})$ each as a linear combination of Legendre polynomials with the G's as coefficients as defined in Appendix (3). Then the integration may be carried out over θ_{A1}, θ_{A2} by the orthogonality relations between the Legendre polynomials. The general result in all three cases M = 0,1, or 2 is that

$$(4.4)\qquad D_{\ell M}(2i_1+1)(2i_2+1)\int_0^{\pi}\int_0^{\pi} P_{i_1}(\cos\theta_{A1}) P_{\ell_1}^{|m_1|}(\cos\theta_{A1})$$

$$\times\, P_{\ell_5}^{|m_5|}(\cos\theta_{A1}) P^{M}(\cos\theta_{A1}) P_{i_2}(\cos\theta_{A2}) P_{\ell_3}^{|m_3|}(\cos\theta_{A2})$$

$$\times\, P_{\ell_6}^{|m_6|}(\cos\theta_{A2}) P^{M}(\cos\theta_{A2}) \sin\theta_{A1} \sin\theta_{A2}\, d\theta_{A1}\, d\theta_{A2}$$

$$= \sum_{\tau_3\,\tau_4} A_{\ell\tau_3\,\tau_4}$$

where $A_{\ell\tau_3\tau_4}$ is a rational function of ℓ. The degree of the numerator is the same as the degree of the denominator, and the upper limits on the summations over τ_3, τ_4 are independent of ℓ. By the orthogonality properties of the Legendre polynomials, i_1, i_2 are no longer independent but become functions of ℓ. Since

$$\lim_{\ell \to \infty} A_{\ell\tau_3\tau_4} = \text{constant} \neq \pm\infty,\ 0$$

by the remarks above, the coefficients $A_{\ell\tau_3\tau_4}$ cannot affect the basic convergence of the series. So integration over Θ_{A1}, Θ_{A2} reduces the series to a linear combination of series of the following type:

$$(4.5) \qquad \sum_{\ell}^{\infty} \int_0^{\infty}\int_0^{\infty} r_{A1}^{\tau_1+\frac{1}{2}} e^{-k_1 r_{A1}} f_{\ell+\tau_3}(k_2, r_{A1}, \rho_B) \times (r_{A<}^{\ell} / r_{A>}^{\ell+1}) \, r_{A2}^{\tau_2+\frac{1}{2}} e^{-k_3 r_{A2}} f_{\ell+\tau_4}(k_4, r_{A2}, \rho_B) \times dr_{A1}\, dr_{A2} \,.$$

As in Part 3, we may take $f_\ell = p_\ell$ (Appendix (2)) and write p_ℓ as a linear combination of $\gamma_{\ell+\tau}$ (Appendix (2)). Then (4.5) reduces to a linear combination of at most four series of the type:

$$(4.6) \qquad \sum_{\ell}^{\infty} \frac{1}{(2\ell+2\tau_3+1)(2\ell+2\tau_4+1)} \int_0^{\infty}\int_0^{\infty} r_{A1}^{\tau_1+\frac{1}{2}} e^{-k_1 r_{A1}} \gamma_{\ell+\tau_5}(k_2, r_{A1}, \rho_B)(r_{A<}^{\ell} / r_{A>}^{\ell+1}) r_{A2}^{\tau_2+\frac{1}{2}} e^{-k_3 r_{A2}} \gamma_{\ell+\tau_6}(k_4, r_{A2}, \rho_B)\, dr_{A1} dr_{A2}$$

where $\tau_5 = \tau_3 \pm 1$, $\tau_6 = \tau_4 \pm 1$.

Noting the definition of $(r_{A<}^{\ell} / r_{A>}^{\ell+1})$ we write (4.6) as a sum of two series, (4.7) and (4.8) where (4.7), (4.8) are given by:

$$(4.7)\qquad \sum_{\ell}^{\infty} \frac{1}{(2\ell+2\tau_3+1)(2\ell+2\tau_4+1)} \int_0^{\infty}\int_0^{r_{A2}} r_{A1}^{\ell+\tau_1+\frac{3}{2}}\, e^{-k_1 r_{A1}}$$
$$\times\ \gamma_{\ell+\tau_5}(k_2, r_{A1}, \rho_B)\, r_{A2}^{-\ell+\tau_2+\frac{1}{2}}\, e^{-k_3 r_{A2}}$$
$$\times\ \gamma_{\ell+\tau_6}(k_4, r_{A2}, \rho_B)\, dr_{A1} dr_{A2}$$

$$(4.8)\qquad \sum_{\ell}^{\infty} \frac{1}{(2\ell+2\tau_3+1)(2\ell+2\tau_4+1)} \int_0^{\infty}\int_{r_{A2}}^{\infty} r_{A1}^{-\ell+\tau_1+\frac{1}{2}}\, e^{-k_1 r_{A1}}$$
$$\times\ \gamma_{\ell+\tau_5}(k_2, r_{A1}, \rho_B)\, r_{A2}^{\ell+\tau_2+\frac{1}{2}}\, e^{-k_3 r_{A2}}$$
$$\times\ \gamma_{\ell+\tau_6}(k_4, r_{A2}, \rho_B)\, dr_{A1} dr_{A2}\ .$$

If in (4.8) we interchange the order of integration,

$$\int_0^{\infty}\int_{r_{A2}}^{\infty} = \int_0^{\infty}\int_0^{r_{A1}} ,$$

we transform (4.8) into a series of the type (4.7) so we need only consider series of type

$$(4.9)\qquad \sum_{\ell}^{\infty} \frac{1}{(2\ell+2\tau_3+1)(2\ell+2\tau_4+1)} S_{\ell} = \sum_{\ell}^{\infty} \frac{1}{(2\ell+2\tau_3+1)(2\ell+2\tau_4+1)} \int_0^{\infty}\int_0^{x}$$
$$y^{\ell+\tau_1+\frac{3}{2}}\, e^{-k_1 y}\, \gamma_{\ell+\tau_5}(k_2, y, \rho_B)\, x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x}\, \gamma_{\ell+\tau_6}(k_4, x, \rho_B)\, dy dx$$

where $y = r_{A1}$, $x = r_{A2}$.

Ignoring the coefficients to the left of the integral signs momentarily, we write S_ℓ as a sum of three integrals $S_\ell = S_\ell^1 + S_\ell^2 + S_\ell^3$ where the integrand of each S_ℓ^j, $j = 1,2,3$ is analytic over the region of integration.

$$(4.10) \qquad S_\ell^1 = \int_0^{\rho_B}\int_0^x y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y} \gamma_{\ell+\tau_5}(k_2,y,\rho_B) \times x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x} \gamma_{\ell+\tau_6}(k_4,x,\rho_B)dydx$$

$$(4.11) \qquad S_\ell^2 = \int_{\rho_B}^{\infty}\int_0^{\rho_B} y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y} \gamma_{\ell+\tau_5}(k_2,y,\rho_B) \times x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x} \gamma_{\ell+\tau_6}(k_4,x,\rho_B)dydx$$

$$= \int_{\rho_B}^{\infty} x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x} \gamma_{\ell+\tau_6}(k_4,x,\rho_B)\, dx \times \int_0^{\rho_B} y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y} \gamma_{\ell+\tau_5}(k_2,y,\rho_B)dy.$$

$$(4.12) \qquad S_\ell^3 = \int_{\rho_B}^{\infty}\int_{\rho_B}^{x} y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y} \gamma_{\ell+\tau_5}(k_2,y,\rho_B) \times x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x} \gamma_{\ell+\tau_6}(k_4,x,\rho_B)dydx$$

$$= \int_{\rho_B}^{\infty}\int_{y}^{\infty} x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x} \gamma_{\ell+\tau_6}(k_4,x,\rho_B)dy \times e^{-k_1 y} \gamma_{\ell+\tau_5}(k_2,y,\rho_B)dxdy.$$

Proceeding as before, by the inequalities of Appendix (4), we can readily deduce the following:

$$(4.13) \qquad S_\ell^1 \geq \frac{\rho_B^{\tau_1+\tau_2+4}\, e^{-(k_1+2k_2+k_3+2k_4)\rho_B}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)(2\ell+\tau_1+\tau_5+3)(2\ell+\tau_1+\tau_5+\tau_6+5)}$$

$$(4.14) \qquad S_\ell^1 \leq \frac{\rho_B^{\tau_1+\tau_2+4}\, e^{(k_4-k_3+(k_2-1)_+)\rho_B}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)(2\ell+\tau_1+\tau_5+3)(2\ell+\tau_1+\tau_2+\tau_5+\tau_6+5)}$$

$$(4.15) \qquad S_\ell^2 \leq \frac{\rho_B^{\tau_1+\tau_2+1}\, e^{(k_4-k_3+(k_2-k_1)_+)\rho_B}}{(2\ell+2\tau_5+1)(2\ell+\tau_1+\tau_5+3)(2\ell+2\tau_6+1)(2\ell-\tau_2+\tau_6-1)}$$

$$(4.16) \qquad S_\ell^3 \leq \frac{\rho_B^{\tau_1+\tau_2}\, e^{(k_2+k_4-k_1-k_3)\rho_B}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)(2\ell-\tau_2+\tau_6-1)(2\ell-\tau_2-\tau_1+\tau_5+\tau_6+1)} .$$

Hence S_ℓ^1 can be both majorized and minorized by terms of the form C^1/ℓ^4 C^1 = constant for large ℓ. Thus S_ℓ^1 behaves asymptotically as C^1/ℓ^4 for large ℓ. Since both S_ℓ^2, S_ℓ^3 are majorized by expressions of the form C^2/ℓ^4, C^3/ℓ^4, where C^2, C^3 are constants it follows that $S_\ell = S_\ell^1 + S_\ell^2 + S_\ell^3$ must behave asymptotically as C/ℓ^4 for large ℓ, C = constant. Therefore it follows that the series (4.9) must behave as C/ℓ^6 for large ℓ if we take into account the coefficients to the left of the integral signs.

5. Three center hybrid-exchange integrals

These are of the form:

$$(5.1)\qquad \int_2 \int_1 \psi_A^{(1)}(1)\psi_B^{(2)}(1) r_{12}^{-1} \psi_A^{(3)}(2)\psi_C^{(4)}(2) dv_1 dv_2$$

$$= C_1C_2C_3C_4 \sum_{\ell=0}^{\infty} \sum_{m=0}^{\ell} D_{\ell m} \int_0^{\infty}\int_0^{\infty}\int_0^{\pi}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}$$

$$\times\, r_{A1}^{n_1+1} e^{-k_1 r_{A1}} r_{B1}^{n_2-1} e^{-k_2 r_{B1}} (r_{A<}^{\ell} / r_{A>}^{\ell+1})\, r_{A2}^{n_3+1} e^{-k_3 r_{A2}}$$

$$\times\, r_{C2}^{n_4-1} e^{-k_4 r_{C2}} P_{\ell_1}^{|m_1|}(\cos\theta_{A1}) P_{\ell_2}^{|m_2|}(\cos\theta_{B1}) P_{\ell}^{m}(\cos\theta_{A1})$$

$$\times\, P_{\ell}^{m}(\cos\theta_{A2}) P_{\ell_3}^{|m_3|}(\cos\theta_{A2}) P_{\ell_4}^{|m_4|}(\cos\theta_{C2}) \sin\theta_{A1}\sin\theta_{A2}$$

$$\times\, \Phi_{m_1}(\phi_{A1})\, \Phi_{m_2}(\phi_{B1}) \cos m(\phi_{A1}-\phi_{A2})\, \Phi_{m_3}(\phi_{A2})\, \Phi_{m_4}(\phi_{C2})$$

$$\times\, d\phi_{A1}\, d\phi_{A2}\, d\theta_{A1}\, d\theta_{A2}\, dr_{A1}\, dr_{A2}\ .$$

We first expand

$$r_{C2}^{\ell_4} P_{\ell_4}^{|m_4|}(\cos\theta_{C2})\, \Phi_{m_4}(\phi_{C2})$$

in terms of r_{A2}, ρ_C, and $P_{\ell_6}^{|m_6|}(\cos\theta_{A2})\, \Phi_{m_6}(\phi_{A2})$ by the expansions given in Appendix (2). Then

$$r_{B1}^{\ell_5}\, P_{\ell_5}^{|m_5|}(\cos\theta_{B1})$$

is expanded in terms of r_{A1}, ρ_B, and $P_{\ell_5}^{|m_5|}(\cos\theta_{A1})$. Here $0 \le |m_i| \le \ell_i \le 1$, $i = 5$ or 6. Next we expand $r_{B1}^{n_2-\ell_2-1} e^{-k_2 r_{B1}}$, $r_{C2}^{n_4-\ell_4-1} e^{-k_4 r_{C2}}$ by the expansions given in Appendix (2). The series (5.1) then becomes a linear combination of at most six series of the form:

$$\text{(5.2)} \quad \sum_{\ell=0}^{\infty} \sum_{m=0}^{\ell} \sum_{i_1=0}^{\infty} \sum_{i_2=0}^{\infty} \sum_{j_2=0}^{i_2} D_{\ell m}(2i_1+1)E_{i_2 j_2} P_{i_2}^{j_2}(\cos \alpha)$$

$$\int_0^{\infty}\int_0^{\infty}\int_0^{\pi}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} r_{A1}^{\tau_1+\frac{1}{2}} e^{-k_1 r_{A1}} f_{i_1}(k_2, r_{A1}, \rho_B)$$

$$\times (r_{A<}^{\ell} / r_{A>}^{\ell+1}) \, r_{A2}^{\tau_2+\frac{1}{2}} e^{-k_3 r_{A2}} f_{i_2}(k_4, r_{A2}, \rho_C)$$

$$\times P_{\ell_1}^{|m_1|}(\cos \theta_{A1}) P_{\ell_5}^{|m_5|}(\cos \theta_{A1}) P_{\ell}^{m}(\cos \theta_{A1}) P_{i_1}(\cos \theta_{A1})$$

$$\times P_{\ell_3}^{|m_3|}(\cos \theta_{A2}) P_{\ell_6}^{|m_6|}(\cos \theta_{A2}) P_{\ell}^{m}(\cos \theta_{A2}) P_{i_2}^{j_2}(\cos \theta_{A2})$$

$$\times \sin \theta_{A1} \sin \theta_{A2} \, \Phi_{m_1}(\phi_{A1}) \, \Phi_{m_2}(\phi_{A1}) \cos m(\phi_{A1}-\phi_{A2})$$

$$\times \Phi_{m_3}(\phi_{A2}) \, \Phi_{m_6}(\phi_{A2}) \cos j_2\phi_{A2} \, d\phi_{A1} d\phi_{A2} \, d\theta_{A1} d\theta_{A2}$$

$$\times dr_{A1} \, dr_{A2}$$

where τ_1, $\tau_2 = 1,2$ or 3, $f_i = p_i$ or q_i, as before.

We expand $\Phi_{m_1} \Phi_{m_2}$ and $\Phi_{m_3} \Phi_{m_6} \cos j_2 \phi_{A2}$ each as a linear combination of sines and cosines. The integral will vanish unless a sine or cosine function in the expansion of $\Phi_{m_1} \Phi_{m_2}$ equals a sine or cosine function in the expansion of $\Phi_{m_3} \Phi_{m_6} \cos j_2 \phi_{A2}$. In the latter case, integration over ϕ_{A1}, ϕ_{A2} transforms (5.2) into a linear combination of at most two series of the form:

(5.3) $$\sum_{\ell=M}^{\infty}\sum_{i_1=0}^{\infty}\sum_{i_2=j}^{\infty} D_{\ell M}(2i_1+1)E_{i_2 j}P_{i_2}^{j}(\cos\alpha)$$

$$\times \int_0^{\infty}\int_0^{\infty}\int_0^{\pi}\int_0^{\pi} r_{A1}^{\tau_1+\frac{1}{2}} e^{-k_1 r_{A1}} f_{i_1}(k_2,r_{A1},\rho_B)(r_{A<}^{\ell} / r_{A>}^{\ell+1})$$

$$\times r_{A2}^{\tau_2+\frac{1}{2}} e^{-k_3 r_{A2}} f_{i_2}(k_4,r_{A2},\rho_C)P_{\ell_1}^{|m_1|}(\cos\theta_{A1})P_{\ell_5}^{|m_5|}(\cos\theta_{A1})$$

$$\times P_{\ell}^{M}(\cos\theta_{A1})P_{i_1}(\cos\theta_{A1})P_{\ell_3}^{|m_3|}(\cos\theta_{A2})P_{\ell_6}^{|m_6|}(\cos\theta_{A2})$$

$$\times P_{\ell}^{M}(\cos\theta_{A2})P_{i_2}^{j}(\cos\theta_{A2})\sin\theta_{A1}\sin\theta_{A2}\, d\theta_{A1}\, d\theta_{A2}\, dr_{A1}dr_{A2}.$$

As before, $M = 0,1,$ or 2 only. Then $j = 0,1,2,3,$ or 4 only. Similarly, we expand $P_{i_2}^{j}(\cos\alpha) = \sin^{-j}\alpha(\sin^{j}\alpha\; P_{i_2}^{j}(\cos\alpha))$ as a linear combination of Legendre polynomials with the G's as coefficients (see Appendix (3)). By the expansions in the same appendix, $P_{\ell_1}^{|m_1|}(\cos\theta_{A1})\; P_{\ell_5}^{|m_5|}(\cos\theta_{A1})P_{\ell}^{M}(\cos\theta_{A1})$ may be written as a linear combination of Legendre polynomials with the G's as coefficients. Next, we expand $P_{\ell_3}^{|m_3|}(\cos\theta_{A2})P_{\ell_6}^{|m_6|}(\cos\theta_{A2})$ $\times P_{\ell}^{M}(\cos\theta_{A2})P_{i_2}^{j}(\cos\theta_{A2})$ as a linear combination of products of two Legendre functions with G's as coefficients. The analysis of all possible cases arising from $M = 0,1,$ or 2, and $j = 0,1,2,3$ or 4 show that

(5.4) $$\sin^{-j}\alpha(\sin^{j}\alpha\; P_{i_2}^{j}(\cos\alpha))D_{\ell M}(2i_1+1)E_{i_2 j}$$

$$\times \int_0^{\pi}\int_0^{\pi} P_{\ell_1}^{|m_1|}(\cos\theta_{A1})P_{\ell_5}^{|m_5|}(\cos\theta_{A1})P_{\ell}^{M}(\cos\theta_{A1})$$

$$\times P_{i_1}(\cos\theta_{A1})P_{\ell_3}^{|m_3|}(\cos\theta_{A2})P_{\ell_6}^{|m_6|}(\cos\theta_{A2})$$

$$\times P_{\ell}^{M}(\cos\theta_{A2})P_{i_2}^{j}(\cos\theta_{A2})\sin\theta_{A1}\sin\theta_{A2}\, d\theta_{A1}d\theta_{A2}$$

$$= \sin^{-j}\alpha \sum_{\tau_8\tau_9\tau_{10}\tau_7} A_{\tau_8\tau_9\tau_{10}\tau_7} P_{\ell+\tau_7}(\cos\alpha)$$

where the $A_{\ell\tau_8\tau_9\tau_{10}\tau_7}$ are rational functions of ℓ the numerator having the same degree as the denominator. The upper limits on the summations over the τ's are independent of ℓ. By the orthogonality properties of the Legendre functions the $i_1 \cdot i_2$ are no longer independent but are functions of ℓ. Since by the above remarks $\lim_{\ell \to \infty} A_{\ell\tau_8\tau_9\tau_{10}\tau_7} = \text{constant} \neq 0$ $\neq \pm\infty$, the coefficients $A_{\ell\tau_8\tau_9\tau_{10}\tau_7}$ do not affect the convergence rate of the basic series of integrals.

Integration over the θ_{A1}, θ_{A2} variables reduces (5.3) to a linear combination of series of the following type:

$$(5.5) \qquad \sum_{\ell}^{\infty} P_{\ell+\tau_7}(\cos\alpha)\int_0^{\infty}\int_0^{\infty} r_{A1}^{\tau_1+\frac{1}{2}} e^{-k_1 r_{A1}} f_{\ell+\tau_3}(k_2, r_{A1}, \rho_B)$$
$$\times (r_{A<}^{\ell} / r_{A>}^{\ell+1}) r_{A2}^{\tau_2+\frac{1}{2}} e^{-k_3 r_{A2}} f_{\ell+\tau_4}(k_4, r_{A2}, \rho_C)\, dr_{A1} dr_{A2}.$$

As with two center exchange integrals we note the only possibilities for the f functions and write (5.5) as a linear combination of four series of the type:

$$(5.6) \qquad \sum_{\ell}^{\infty} \frac{1}{(2\ell+2\tau_3+1)(2\ell+2\tau_4+1)} P_{\ell+\tau_7}(\cos\alpha)\int_0^{\infty}\int_0^{\infty} r_{A1}^{\tau_1+\frac{3}{2}} e^{-k_1 r_{A1}}$$
$$\times \gamma_{\ell+\tau_5}(k_2, r_{A1}, \rho_B)(r_{A<}^{\ell} / r_{A>}^{\ell+1}) r_{A2}^{\tau_2+\frac{3}{2}} e^{-k_3 r_{A2}} \gamma_{\ell+\tau_6}(k_4, r_{A2}, \rho_C)$$
$$\times dr_{A1}\, dr_{A2} \quad \text{where} \quad \tau_5 = \tau_3 \pm 1, \quad \tau_6 = \tau_4 \pm 1.$$

Noting the definition of $(r_{A<}^{\ell} / r_{A>}^{\ell+1})$ we write (5.6) as a sum of two series, (5.7), (5.8) where (5.7), (5.8) are given by

$$(5.7) \qquad \frac{P_{\ell+\tau_1}(\cos\alpha)}{(2\ell+2\tau_3+1)(2\ell+2\tau_4+1)} \int_0^\infty \int_0^{r_{A2}} r_{A1}^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 r_{A1}}$$

$$\times \gamma_{\ell+\tau_5}(k_2, r_{A1}, \rho_B) r_{A2}^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 r_{A2}} \gamma_{\ell+\tau_6}(k_4, r_{A2}, \rho_C) dr_{A1} dr_{A2}$$

$$(5.8) \qquad \frac{P_{\ell+\tau_7}(\cos\alpha)}{(2\ell+2\tau_3+1)(2\ell+2\tau_4+1)} \int_0^\infty \int_{r_{A2}}^\infty r_{A1}^{-\ell+\tau_1+\frac{1}{2}} e^{-k_1 r_{A1}}$$

$$\times \gamma_{\ell+\tau_5}(k_2, r_{A1}, \rho_B) r_{A2}^{\ell+\tau_2+\frac{3}{2}} e^{-k_3 r_{A2}} \gamma_{\ell+\tau_6}(k_4, r_{A2}, \rho_C) dr_{A1} dr_{A2}.$$

Interchanging the order of integration in (5.8),

$$\int_0^\infty \int_{r_{A2}}^\infty = \int_0^\infty \int_0^{r_{A1}},$$

transforms the series (5.8) into a series of type (5.7), so we need consider only series of type (5.7), namely,

$$(5.9) \qquad \sum_{\ell}^{\infty} \frac{P_{\ell+\tau_1}(\cos\alpha)}{(2\ell+2\tau_3+1)(2\ell+2\tau_4+1)} S_\ell$$

$$= \sum_{\ell}^{\infty} \frac{P_{\ell+\tau_1}(\cos\alpha)}{(2\ell+2\tau_3+1)(2\ell+2\tau_4+1)} \int_0^\infty \int_0^x y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y}$$

$$\times \gamma_{\ell+\tau_5}(k_2, y, \rho_B)\, x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x} \gamma_{\ell+\tau_6}(k_4, x, \rho_C)$$

$$\times\, dy\, dx \qquad \text{where } x = r_{A2}, \qquad y = r_{A1}.$$

We now must consider three cases $\rho_B < \rho_C$, $\rho_B > \rho_C$, and $\rho_B = \rho_C$.

<u>Case 1</u>, $\rho_B < \rho_C$:

Ignoring the coefficient to the left of the integral signs, we

write $S_\ell = S_\ell^1 + S_\ell^2 + S_\ell^3 + S_\ell^4 + S_\ell^5 + S_\ell^6$ where in each S_ℓ^j the integrand is analytic over the region of integration.

$$(5.10) \qquad S_\ell^1 = \int_0^{\rho_B}\int_0^x y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y} \gamma_{\ell+\tau_5}(k_2,y,\rho_B) x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x} \times \gamma_{\ell+\tau_6}(k_4,x,\rho_C)\,dy\,dx$$

$$(5.11) \qquad S_\ell^2 = \int_{\rho_B}^{\rho_C} x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x} \gamma_{\ell+\tau_6}(k_4,x,\rho_C)\,dx \times \int_0^{\rho_B} y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y} \gamma_{\ell+\tau_5}(k_2,y,\rho_B)\,dy$$

$$(5.12) \qquad S_\ell^3 = \int_{\rho_B}^{\rho_C}\int_{\rho_B}^{x} y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y} \gamma_{\ell+\tau_5}(k_2,y,\rho_B) \times x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x} \gamma_{\ell+\tau_6}(k_4,x,\rho_C)\,dy\,dx$$

$$(5.13) \qquad S_\ell^4 = \int_{\rho_C}^{\infty} x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x} \gamma_{\ell+\tau_6}(k_4,x,\rho_C)\,dx \times \int_0^{\rho_B} y^{\ell+\tau_1+\frac{1}{2}} e^{-k_1 y} \gamma_{\ell+\tau_5}(k_2,y,\rho_B)\,dy$$

$$(5.14) \qquad S_\ell^5 = \int_{\rho_C}^{\infty} x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x} \gamma_{\ell+\tau_6}(k_4,x,\rho_C)\,dx \times \int_{\rho_B}^{\rho_C} y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y} \gamma_{\ell+\tau_5}(k_2,y,\rho_B)\,dy$$

$$(5.15)\qquad S_\ell^6 = \int_{\rho_C}^{\infty}\int_{y}^{\infty} x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x}\gamma_{\ell+\tau_6}(k_4,x,\rho_C)$$

$$\times y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y}\gamma_{\ell+\tau_5}(k_2,y,\rho_B)\,dxdy.$$

From the inequalities of Appendix (4) we can readily deduce the following:

$$(5.16)\qquad S_\ell^1 \geq \frac{e^{-(k_1+2k_2+k_3+k_4)\rho_B} e^{-k_4\rho_C} \rho_B^{\frac{9}{2}+\tau_1+\tau_2+\tau_5} \rho_C^{-\tau_6-\frac{1}{2}}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)(2\ell+\tau_1+\tau_5+3)(2\ell+\tau_1+\tau_2+\tau_5+\tau_6+5)}\left(\frac{\rho_B}{\rho_C}\right)^\ell$$

$$(5.17)\qquad S_\ell^1 \leq \frac{e^{(k_4-k_3+(k_2-k_1)_+)_+\rho_B} \rho_B^{\frac{9}{2}+\tau_1+\tau_2+\tau_5} \rho_C^{-\tau_6-\frac{1}{2}}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)(2\ell+\tau_1+\tau_5+3)(2\ell+\tau_1+\tau_2+\tau_5+\tau_6+5)}\left(\frac{\rho_B}{\rho_C}\right)^\ell$$

$$(5.18)\qquad S_\ell^2 \geq \frac{e^{-(k_1+2k_2)\rho_B} e^{-k_4\rho_C} \rho_B^{\tau_5+\frac{1}{2}} \rho_C^{-\tau_6-\frac{1}{2}}}{(2\ell+2\tau_6+1)(2\ell+2\tau_5+1)(2\ell+\tau_1+\tau_5+3)}\left(\frac{\rho_B}{\rho_C}\right)^\ell \int_{\rho_B}^{\rho_C} x^{\tau_2+\tau_6+1} e^{-(k_3+k_4)x}\,dx$$

$$(5.19)\qquad S_\ell^2 \leq \frac{e^{(k_2-k_1)\rho_B} \rho_B^{\tau_1+\frac{1}{2}} \rho_C^{-\tau_6-\frac{1}{2}}}{(2\ell+2\tau_6+1)(2\ell+2\tau_5+1)(2\ell+\tau_1+\tau_5+3)}\left(\frac{\rho_B}{\rho_C}\right)^\ell \int_{\rho_B}^{\rho_C} x^{\tau_2+\tau_6+1} e^{(k_4-k_3)x}\,dx$$

$$(5.20)\qquad S_\ell^3 \geq \frac{e^{-k_2\rho_B} e^{-k_4\rho_C} \rho_B^{\tau_5+\frac{1}{2}} \rho_C^{-\tau_6-\frac{1}{2}}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)}\left(\frac{\rho_B}{\rho_C}\right)^\ell$$

$$\times \int_{\rho_B}^{\rho_C}\int_{\rho_B}^{x} y^{\tau_1-\tau_5+1} e^{-(k_1+k_2)y} x^{\tau_2+\tau_6+1} e^{-(k_3+k_4)x}\,dydx$$

$$(5.21)\qquad S_\ell^3 \leq \frac{\rho_B^{\tau_5+\frac{1}{2}} \rho_C^{-\tau_6-\frac{1}{2}}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)}\left(\frac{\rho_B}{\rho_C}\right)^\ell$$

$$\times \int_{\rho_B}^{\rho_C}\int_{\rho_B}^{x} y^{\tau_1-\tau_5+1} e^{-(k_1+k_2)y} x^{\tau_2+\tau_6+1} e^{-(k_3+k_4)x}\,dydx$$

(5.22) $$S_\ell^4 \le \frac{e^{(k_4-k_3+(k_2-k_1)_+)\rho_C}\,\rho_B^{\tau_1+\frac{3}{2}}\,\rho_C^{\tau_2+\frac{3}{2}}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)(2\ell+\tau_6-\tau_2-1)(2\ell+\tau_1+\tau_5+3)}\left(\frac{\rho_B}{\rho_C}\right)^\ell$$

(5.23) $$S_\ell^5 \le \frac{e^{k_2\rho_B}e^{(k_4-k_3)\rho_C}\,\rho_B^{\tau_5+\frac{3}{2}}\,\rho_C^{\tau_2+\frac{3}{2}}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)(2\ell+\tau_6-\tau_2+1)}\left(\frac{\rho_B}{\rho_C}\right)^\ell \int_{\rho_B}^{\rho_C} y^{\tau_1-\tau_5+1}e^{-k_1y}\,dy$$

(5.24) $$S_\ell^6 \le \frac{e^{k_2\rho_B}e^{(k_4-k_1-k_2)\rho_C}\,\rho_B^{\tau_5+\frac{1}{2}}\,\rho_C^{\tau_1+\tau_2-\tau_5+\frac{7}{2}}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)(2\ell-\tau_2+\tau_6+1)(2\ell+\tau_6-\tau_2+\tau_5-\tau_1-3)}\left(\frac{\rho_B}{\rho_C}\right)^\ell$$

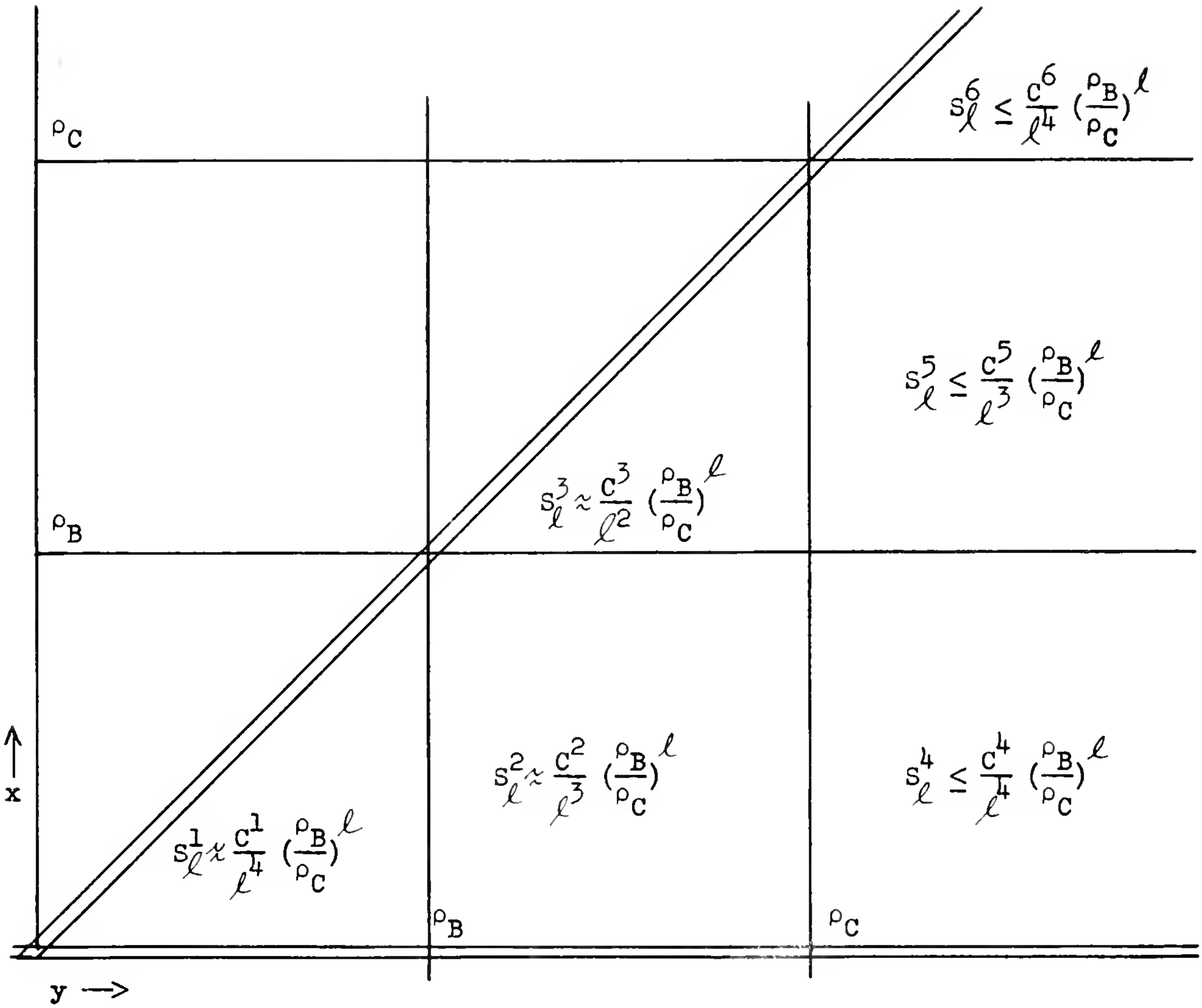
We summarize the asymptotic behavior of the S_ℓ^j for large ℓ as a result of these inequalities in Figure 3. From this we deduce that the asymptotic behavior for large ℓ of S_ℓ is as $\frac{C}{\ell^2}\left(\frac{\rho_B}{\rho_C}\right)^\ell$ C = constant. Hence the absolute asymptotic behavior for large ℓ of the terms of series (5.9), taking into account the coefficients to the left of the integral signs is as $\frac{C}{\ell^{9/2}}\left(\frac{\rho_B}{\rho_C}\right)^\ell$.

<u>Case 2</u>: $\rho_B > \rho_C$

We again write $S_\ell = S_\ell^1 + S_\ell^2 + S_\ell^3 + S_\ell^4 + S_\ell^5 + S_\ell^6$ where now

(5.25) $$S_\ell^1 = \int_0^{\rho_C}\int_0^x y^{\ell+\tau_1+\frac{3}{2}}e^{-k_1y}\gamma_{\ell+\tau_5}(k_2,y,\rho_B) \times x^{-\ell+\tau_2+\frac{1}{2}}e^{-k_3x}\gamma_{\ell+\tau_6}(k_4,x,\rho_C)\,dy\,dx$$

(5.26) $$S_\ell^2 = \int_{\rho_C}^{\rho_B} x^{-\ell+\tau_2+\frac{1}{2}}e^{-k_3x}\gamma_{\ell+\tau_6}(k_4,x,\rho_C)\,dx \times \int_0^{\rho_C} y^{\ell+\tau_1+\frac{3}{2}}e^{-k_1y}\gamma_{\ell+\tau_5}(k_2,y,\rho_B)\,dy$$



The C^j are constants.

The double lines bound the region of integration;

$$0 \le x < +\infty,$$

$0 \le y \le x$

FIGURE 3.

$$(5.27)\qquad S_\ell^3 = \int_{\rho_C}^{\rho_B}\int_{\rho_C}^{x} y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y}\gamma_{\ell+\tau_5}(k_2,y,\rho_B) \times x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x}\gamma_{\ell+\tau_6}(k_4,x,\rho_C)\,dy\,dx$$

$$(5.28)\qquad S_\ell^4 = \int_{\rho_B}^{\infty} x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x}\gamma_{\ell+\tau_6}(k_4,x,\rho_C)\,dx \times \int_{0}^{\rho_B} y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y}\gamma_{\ell+\tau_5}(k_2,y,\rho_B)\,dy$$

$$(5.29)\qquad S_\ell^5 = \int_{\rho_B}^{\infty} x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x}\gamma_{\ell+\tau_6}(k_4,x,\rho_C)\,dx \times \int_{\rho_C}^{\rho_B} y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y}\gamma_{\ell+\tau_5}(k_2,y,\rho_B)\,dy$$

$$(5.30)\qquad S_\ell^6 = \int_{\rho_B}^{\infty}\int_{y}^{\infty} x^{-\ell+\tau_2+\frac{1}{2}} e^{-k_3 x}\gamma_{\ell+\tau_6}(k_4,x,\rho_C) \times y^{\ell+\tau_1+\frac{3}{2}} e^{-k_1 y}\gamma_{\ell+\tau_5}(k_2,y,\rho_B)\,dx\,dy.$$

From the inequalities of Appendix (4) we can readily deduce the following:

$$(5.31)\qquad S_\ell^1 \geq \frac{e^{-k_2\rho_B} e^{-(k_1+2k_2+k_3+2k_4)\rho_C}\,\rho_B^{-\tau_5-\frac{1}{2}}\,\rho_C^{\tau_1+\tau_2+\tau_6+\frac{9}{2}}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)(2\ell+\tau_1+\tau_5+3)(2\ell+\tau_1+\tau_2+\tau_5+\tau_6+5)}\left(\frac{\rho_C}{\rho_B}\right)^{\ell}$$

$$s_\ell^1 \leq \frac{e^{(k_4-k_3+(k_2-k_1)_+)_+\rho_C}\,\rho_B^{-\tau_5-\frac{1}{2}}\,\rho_C^{\tau_1+\tau_2+\tau_6+\frac{9}{2}}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)(2\ell+\tau_1+\tau_5+3)(2\ell+\tau_1+\tau_2+\tau_5+\tau_6+5)}\left(\frac{\rho_C}{\rho_B}\right)^\ell \tag{5.32}$$

$$s_\ell^2 \geq \frac{e^{-(k_2+k_3+k_4)\rho_B}\,e^{-(k_1+k_2+k_4)\rho_C}\,\rho_B^{-\tau_5-\frac{1}{2}}\,\rho_C^{\frac{9}{2}+\tau_1+\tau_2+\tau_5}}{(2\ell+2\tau_5+1)(2\ell+\tau_1+\tau_5+3)(2\ell+2\tau_6+1)(2\ell+\tau_6-\tau_2-1)}\left(\frac{\rho_C}{\rho_B}\right)^\ell \times\left[1-\left(\frac{\rho_C}{\rho_B}\right)^{2\ell+\tau_6-\tau_2-1}\right] \tag{5.33}$$

$$s_\ell^2 \leq \frac{e^{((k_2-k_1)_+-k_3)\rho_C}\,\rho_B^{-\tau_5-\frac{1}{2}}\,\rho_C^{\frac{9}{2}+\tau_1+\tau_2+\tau_5}}{(2\ell+2\tau_5+1)(2\ell+\tau_1+\tau_5+3)(2\ell+2\tau_6+1)(2\ell+\tau_6-\tau_2-1)}\left(\frac{\rho_C}{\rho_B}\right)^\ell \times\left[1-\left(\frac{\rho_C}{\rho_B}\right)^{2\ell+\tau_6-\tau_2-1}\right]. \tag{5.34}$$

$$s_\ell^3 \geq \frac{e^{-k_2\rho_B}\,e^{-(k_1+k_2+2k_3+k_4)\rho_C}\,\rho_C^{\tau_6+\frac{1}{2}}\,\rho_B^{-\tau_5-\frac{1}{2}}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)(2\ell+\tau_1+\tau_5+3)}\left(\frac{\rho_C}{\rho_B}\right)^\ell \times\left[\frac{\rho_B^{\tau_1+\tau_5+\tau_2-\tau_6+4}-\rho_C^{\tau_1+\tau_5+\tau_2-\tau_6+4}}{(\tau_1+\tau_5+\tau_4-\tau_6+4)} - \frac{\rho_C^{\tau_1+\tau_2+\tau_5-\tau_6+4}}{(2\ell+\tau_2-\tau_6-1)}\left[\left(\frac{\rho_C}{\rho_B}\right)^{2\ell-\tau_2+\tau_6-1}-1\right]\right]. \tag{5.35}$$

$$s_\ell^3 \leq \frac{e^{(k_2-k_1)_+\rho_B}\,e^{(k_4-k_2+(k_2-k_1)_+)\rho_C}\,\rho_C^{\tau_6+\frac{1}{2}}\,\rho_B^{-\tau_5-\frac{1}{2}}}{(2\ell+2\tau_5+1)(2\ell+2\tau_6+1)(2\ell+\tau_1+\tau_5+3)}\left(\frac{\rho_C}{\rho_B}\right)^\ell \times\left[\frac{\rho_B^{\tau_1+\tau_5+\tau_2-\tau_6+4}-\rho_C^{\tau_1+\tau_5+\tau_2-\tau_6+4}}{(\tau_1+\tau_5+\tau_4-\tau_6+4)} - \frac{\rho_C^{\tau_1+\tau_2+\tau_5-\tau_6+4}}{(2\ell+\tau_2-\tau_6-1)}\left[\left(\frac{\rho_C}{\rho_B}\right)^{2\ell-\tau_2+\tau_6-1}-1\right]\right] \tag{5.36}$$

$$(5.37)\qquad S_\ell^4 \le \frac{e^{(k_4+(k_2-k_1)_+)\rho_C}\,\rho_C^{\tau_1+\tau_5+\tau_6+\frac{7}{2}}\,\rho_B^{-\tau_6+\tau_2+1}}{(2\ell+2\tau_6+1)(2\ell+\tau_6-\tau_2-1)(2\ell+2\tau_5+1)(2\ell+\tau_1+\tau_5+3)}\left(\frac{\rho_C}{\rho_B}\right)^{3\ell}$$

$$(5.38)\qquad S_\ell^5 \le \frac{e^{(k_4-(k_2-k_1)_-)\rho_C}\,e^{(k_2-k_1)_+\rho_B-k_3)\,\rho_B}\,\rho_C^{\tau_6+\frac{1}{2}}\,\rho_B^{\tau_1+\tau_2-\tau_5-\tau_6+4}}{(2\ell+2\tau_5+1)(2\ell+\tau_1+3)(2\ell+2\tau_6+1)(2\ell+\tau_6-\tau_2-1)}\left(\frac{\rho_C}{\rho_B}\right)^{\ell}$$

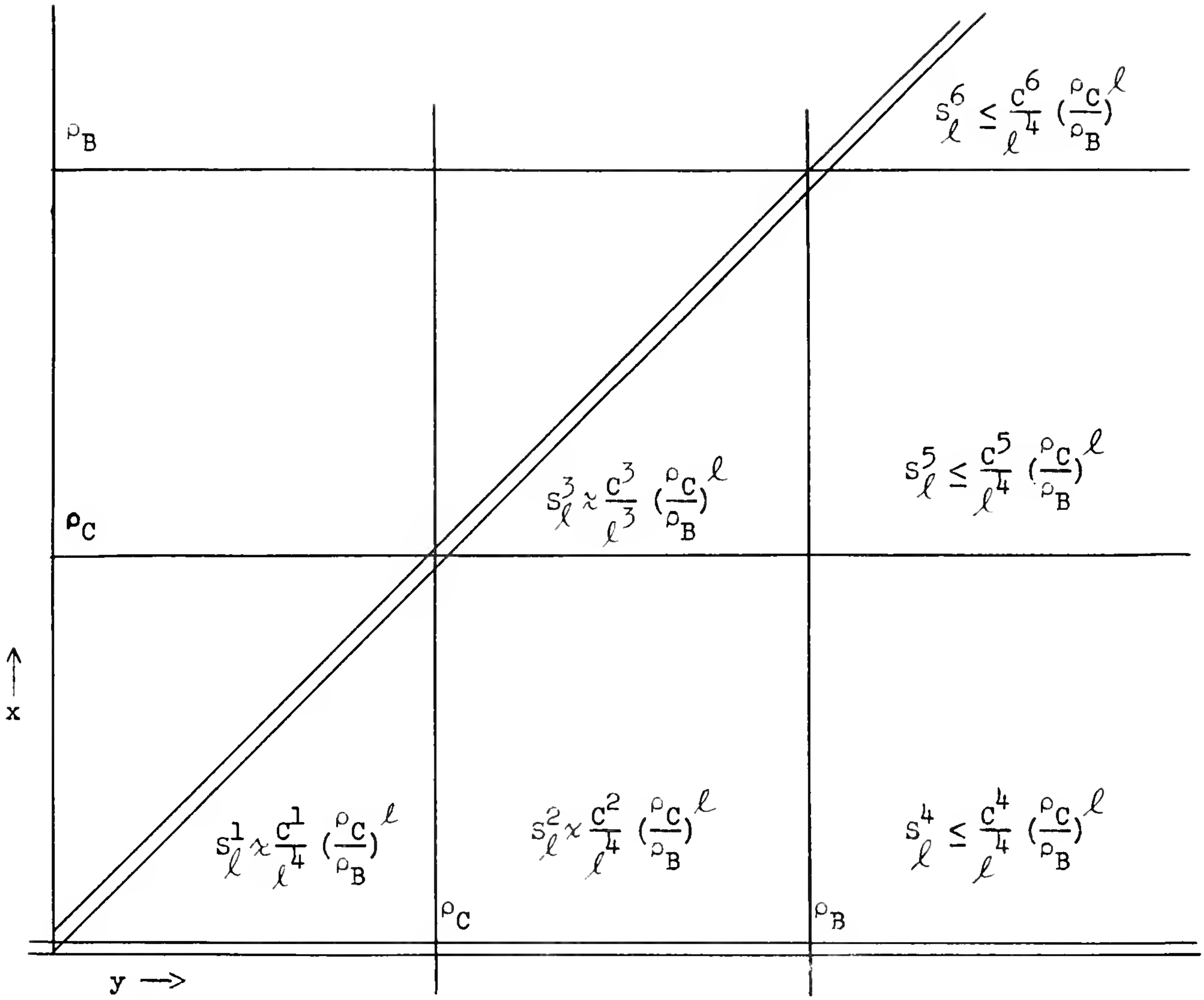
$$(5.39)\qquad S_\ell^6 \le \frac{e^{(k_2-k_1-k_3)\rho_B}\,e^{k_4\rho_C}\,\rho_B^{\tau_1+\tau_2-\tau_6+\frac{1}{2}}\,\rho_C^{\tau_6+\frac{1}{2}}}{(2\ell+2\tau_5+1)(2\ell+2\tau_7+1)(2\ell-\tau_2+\tau_6-1)(2\ell+\tau_6+\tau_5-\tau_1-\tau_2-3)}\left(\frac{\rho_C}{\rho_B}\right)^{\ell}.$$

From these inequalities we can conclude the following asymptotic for large ℓ summarized in Figure 4.

From this we conclude that the asymptotic behavior for large ℓ of S_ℓ is as $\frac{C}{\ell^3}\left(\frac{\rho_C}{\rho_B}\right)$ C = constant. Hence the absolute asymptotic behavior for large ℓ of the terms of the series (5.9) is as $\frac{C}{\ell^{11/2}}\left(\frac{\rho_C}{\rho_B}\right)$ taking into account the coefficients to the left of the ingegral signs.

<u>Case 3</u>: $\rho_B = \rho_C$

Here $S_\ell^2 = S_\ell^3 = S_\ell^5 = 0$; and hence the absolute asymptotic behavior of the terms of the series (5.9) can be shown to be as $\frac{C}{\ell^{13/2}}$.



The C^j are constants.

The double lines bound the region of integration;

$$0 \leq x < +\infty;$$

$0 \leq y \leq x$.

FIGURE 4.

6. Three center coulomb-exchange integrals

These are of the form:

$$(6.1)\qquad \int_2\int_1 \psi_B^{(1)}(1)\psi_B^{(2)}(1)\, r_{12}^{-1}\, \psi_A^{(3)}(2)\psi_C^{(4)}(2)\, dv_1 dv_2 .$$

The analysis of these integrals is identical to that of the hybrid exchange integrals. The results of the analysis are the same as those for hybrid-exchange integrals except in the case in which $\psi_B^{(1)}(1) = \psi_B^{(2)}(1) = \psi_{2,0,0,b}(1)$ (see Appendix (1)). Here the reduction of the integrals to the series (5.2) is identical to that of the hybrid-exchange integrals, but in series (5.5) $f_{\ell+\tau_3}$ no longer equals $p_{\ell+\tau_3}$ or $q_{\ell+\tau_3}$, but equals $\zeta_{3,\ell+\tau_3}$ (see Appendix (2)). The expansion of $\zeta_{3,\ell+\tau_3}$ in terms of $\gamma_{\ell+\tau_5}$ gives rise to linear combinations of γ's of the form:

$$(6.2)\qquad \frac{1}{(2\ell+2\tau_3+1)(2\ell+2\tau+1)}\,\gamma_{\ell+\tau_5} .$$

So an extra factor of $\frac{1}{(2\ell+2\tau_3+1)}$ into the series of (5.9) is introduced.

A summary of the asymptotic behavior of the series (5.9) in this case is given here:

1. $\rho_B < \rho_C$

   The terms of series (5.9) behave absolutely asymptotically as $\frac{C}{\ell^{11/2}} \left(\frac{\rho_B}{\rho_C}\right)^{\ell}$ for large ℓ.

2. $\rho_B > \rho_C$

   The terms of series (5.9) behave absolutely asymptotically as $\frac{C}{\ell^{13/2}} \left(\frac{\rho_C}{\rho_B}\right)^{\ell}$ for large ℓ.

3. $\rho_B = \rho_C$

   The terms of series (5.9) behave absolutely asymptotically as $\frac{C}{\ell^{15/2}}$ for large ℓ .

Appendix (1)

A general Slater function[6] denoted by $\psi_{n,\ell,m;\mu}(r_{\mu\delta},\theta_{\mu\delta},\phi_{\mu\delta};k)$ is given by

$$C(n,\ell,m;k)\, r_{\mu\delta}^{n-1}\, e^{-kr_{\mu\delta}}\, P_{\ell}^{|m|}(\cos\theta_{\mu\delta})\, \Phi_m(\phi_{\mu\delta})$$

where k is a positive real number; n, ℓ, m are integers satisfying $0 \le \ell < n$ and $0 \le |m| \le \ell$; μ = A,B, or C; and δ = 1 or 2.

$$C(n,\ell,m;k) = (2k)^{n+\frac{1}{2}} \left[\frac{(2\ell+1)(\ell-|m|)!}{2\pi(\ell+|m|)!(2n)!} \right]^{1/2}$$

and $\Phi_m(\phi) = \cos m\phi$ for $m > 0$, $\Phi_0(\phi) = \frac{1}{\sqrt{2}}$, and $\Phi_m(\phi) = -\sin m\phi$ for $m < 0$.

Throughout this paper we restrict ourselves to Slater functions with n = 1 or 2 only. These are the following five functions:

$$\psi_{1,0,0;\mu}(r_{\mu\delta},\theta_{\mu\delta},\phi_{\mu\delta};k) = (k^3/\pi)^{1/2}\, e^{-kr_{\mu\delta}}$$

$$\psi_{2,0,0;\mu}(r_{\mu\delta},\theta_{\mu\delta},\phi_{\mu\delta};k) = (k^5/3\pi)^{1/2}\, r_{\mu\delta}\, e^{-kr_{\mu\delta}}$$

$$\psi_{2,1,0;\mu}(r_{\mu\delta},\theta_{\mu\delta},\phi_{\mu\delta};k) = (k^5/\pi)^{1/2} r_{\mu\delta}\, e^{-kr_{\mu\delta}} \cos\theta_{\mu\delta}$$

$$\psi_{2,1,1;\mu}(r_{\mu\delta},\theta_{\mu\delta},\phi_{\mu\delta};k) = (k^5/\pi)^{1/2} r_{\mu\delta}\, e^{-kr_{\mu\delta}} \cos\theta_{\mu\delta} \cos\phi_{\mu\delta}$$

$$\psi_{2,1,-1;\mu}(r_{\mu\delta},\theta_{\mu\delta},\phi_{\mu\delta};k) = (k^5/\pi)^{1/2} r_{\mu\delta}\, e^{-kr_{\mu\delta}} \cos\theta_{\mu\delta} \sin\phi_{\mu\delta}\ .$$

These are denoted by $\psi_{\mu}^{(i)}(\delta)$, for convenience, and the constants $C(n,\ell,m;k)$ are denoted by C_i.

The expansion for r_{12}^{-1} is given as follows[3]:

$$r_{12}^{-1} = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\ell} D_{\ell m}(r_{A<}^{\ell} / r_{A>}^{\ell+1})\ P_{\ell}^{m}(\cos\ \theta_{A1}) P_{\ell}^{m}(\cos\ \theta_{A2}) \cos\ m(\phi_{A1}-\phi_{A2})$$

where $D_{\ell 0} = 1$, $D_{\ell m} = 2\,\frac{(\ell-m)!}{(\ell+m)!}$, $m \neq 0$; $r_{A<} = \min(r_{A1}, r_{A2})$, $r_{A>} = \max(r_{A1}, r_{A2})$.

dv_{δ}, $\delta = 1$ or 2 is given as follows:

$$dv_{\delta} = r_{A\delta}^{2} \sin\ \theta_{A\delta}\ dr_{A\delta}\ d\theta_{A\delta}\ d\phi_{A\delta}.$$

The $P_{\ell}^{m}(\cos\ \theta)$ are the standard Legendre functions [2].

Appendix (2)

The formulas used to expand functions with arguments (r_B, θ_B, ϕ_B) and (r_C, θ_C, ϕ_C) in terms of functions with arguments (r_A, θ_A, ϕ_A) are the following:

$$\phi_B = \phi_A$$

$$r_B \sin \theta_B = r_A \sin \theta_A$$

$$r_B \cos \theta_B = \rho_B - r_A \cos \theta_A$$

$$r_B^{-1} = \sum_{i=0}^{\infty} (\rho_{B<}^{i} / \rho_{B>}^{i+1})\, P_i(\cos \theta_A)$$

$$r_B^{n-1}\, e^{-kr_B} = (\rho_B r_A)^{-1/2} \sum_{i=0}^{\infty} E_{io} P_i(\cos \theta_A)\, \zeta_{ni}(k, r_A, \rho_B)$$

$$r_C \sin \theta_C \sin \phi_C = r_A \sin \theta_A \sin \phi_A$$

$$r_C \sin \theta_C \cos \phi_C = r_A(\cos \alpha \sin \theta_A \cos \phi_A + \sin \alpha \cos \theta_A)$$

$$r_C \cos \theta_C = \rho_C - r_A(-\sin \alpha \sin \theta_A \cos \phi_A + \cos \alpha \cos \theta_A)$$

$$r_C^{-1} = \sum_{i=0}^{\infty} \sum_{j=0}^{i} E'_{ij} (\rho_{C<}^{i} / \rho_{C>}^{i+1}) P_i^j(\cos \alpha) P_i^j(\cos \theta_A) \cos j\phi$$

$$r_C^{n-1}\, e^{-kr_C} = (\rho_C r_A)^{-1/2} \sum_{i=0}^{\infty} \sum_{j=0}^{i} E_{ij} P_i^j(\cos\alpha) P_i^j(\cos\theta_A) \cos j\phi_A \zeta_{ni}(k, r_A, \rho_C).$$

Here: $\rho_{\mu <} = \min(\rho_\mu, r_A)$; $\rho_{\mu >} = \max(\rho_\mu, r_A)$, $\mu = B$ or C

$$E'_{io} = 1; \quad E'_{ij} = 2(i-j)! / (i+j)! \qquad j \neq 0$$

$$E_{io} = 2i+1; \quad E_{ij} = 2(2i+1)(i-j)! / (i+j)! \quad j \neq 0$$

$$\zeta_{ni}(k,r_A,\rho) = \frac{\partial n}{\partial(-k)^n}\,(\gamma_i(k,r_A,\rho))$$

$$\gamma_i(k,r_A,\rho) = I_{i+\frac{1}{2}}(kr_A)K_{i+\frac{1}{2}}(k\rho) \qquad r_A \le \rho$$

$$= I_{i+\frac{1}{2}}(k\rho)\,K_{i+\frac{1}{2}}(kr_A) \qquad r_A > \rho.$$

$I_{i+\frac{1}{2}}$ and $K_{i+\frac{1}{2}}$ are the standard Bessel functions of imaginary argument and half integral orders. For convenience, $\zeta_{1i}(k,r_A,\rho)$ and $\zeta_{2i}(k,r_A,\rho)$ are denoted by $p_i(k,r_A,\rho)$ and $q_i(k,r_A,\rho)$ respectively, sometimes written p_i or q_i for convenience.

The expansions relating functions of (r_C,θ_C,ϕ_C) to those of (r_A,θ_A,ϕ_A) are easily derived from those relating functions of (r_B,θ_B,ϕ_B) to those of (r_A,θ_A,ϕ_A). The latter expansions [1,8] easily follow from the elementary properties of Bessel functions and Legendre polynomials.

Some relations [1] between p_i, q_i, γ_i and ζ_{3i} used in this paper are given here.

$$p_i(k,r_A,\rho) = \frac{kr_A\rho}{2i+1}\left[\gamma_{i-1}(k,r_A,\rho) - \gamma_{i+1}(k,r_A,\rho)\right]$$

$$q_i(k,r_A,\rho) = \frac{kr_A\rho}{2i+1}\left[p_{i-1}(k,r_A,\rho) - p_{i+1}(k,r_A,\rho)\right] - k^{-1}\,p_i(k,r_A,\rho)$$

$$\zeta_{3i}(k,r_A,\rho) = \frac{2r_A\rho}{2i+1}\left[p_{i-1}(k,r_A,\rho)-p_{i+1}(k,r_A,\rho)\right]$$

$$- \frac{kr_A\rho}{2i+1}\left[q_{i-1}(k,r_A,\rho)-q_{i+1}(k,r_A,\rho)\right].$$

Appendix (3)

The following formulas are used to integrate over the θ_{A1}, θ_{A2} variables in the integrals. They consist essentially of expansions for $\sin^N\theta \cos^M\theta P_n^N(\cos\theta)$ N, M, n non-negative integers in terms of linear combinations of Legendre polynomials, and formulas for expanding $\sin\theta\, P_n^N(\cos\theta)$ and $\cos\theta\, P_n^N(\cos\theta)$ in terms of Legendre functions $P_n^{N'}(\cos\theta)$ of lower upper index N'. They can easily be derived from the recurrence relations for Legendre functions and their differential equations [2].

The general expansion formula is

$$\sin^N\theta \cos^M\theta\, P_n^N(\cos\theta) = \sum_{i=0}^{N+M} G_{nMNi}\, P_{n-N-M+2i}(\cos\theta)$$

where the G_{nMNi} (written G for short) are rational functions of n. The first 13 G's are listed here:

$$G_{n100} = \frac{n}{2n+1} \qquad G_{n101} = \frac{n+1}{2n+1}$$

$$G_{n010} = \frac{n(n+1)}{2n+1} \qquad G_{n011} = -\frac{n(n+1)}{2n+1}$$

$$G_{n200} = \frac{n(n-1)}{(2n-1)(2n+1)} \qquad G_{n201} = \frac{2n^2+2n-1}{(2n-1)(2n+3)} \qquad G_{n202} = \frac{(n+1)(n+2)}{(2n+1)(2n+3)}$$

$$G_{n110} = \frac{n(n-1)(n+1)}{(2n-1)(2n+1)} \qquad G_{n111} = \frac{n(n+1)}{(2n-1)(2n+3)} \qquad G_{n112} = \frac{-n(n+1)(n+2)}{(2n+1)(2n+3)}$$

$$G_{n020} = \frac{(n-1)n(n+1)(n+2)}{(2n-1)(2n+1)} \qquad G_{n021} = \frac{(n-1)n(n+1)(n+2)}{(2n-1)(2n+3)} \qquad G_{n022} = \frac{(n-1)n(n+1)(n+2)}{(2n+1)(2n+3)}$$

In general:

$$G_{nMNi} = \frac{(\text{Polynomial in n of degree} \leq M+2N)}{(\text{Polynomial in n of degree} = M+N)} \; .$$

In particular:

$$G_{nMNj} = \frac{(\text{Polynomial in n of degree} = M+2N)}{(\text{Polynomial in n of degree} = M+N)} \quad j = 0 \text{ or } N+M.$$

In addition we shall use the following formulas:

$$\sin\theta\, P_n^{n+1}(\cos\theta) + 2N\cos\theta\, P_n^N(\cos\theta)$$
$$+ (n-N+1)(n+N)\sin\theta\, P_n^{N-1}(\cos\theta) = 0$$

$$\cos\theta\, P_n^N(\cos\theta) = G_{n100}\, P_{n-1}^N(\cos\theta) + G_{n101} P_{n+1}^N(\cos\theta)$$
$$- N\sin\theta\, P_n^{N-1}(\cos\theta).$$

Appendix (4)

We shall derive some simple inequalities for the Bessel functions $I_{n+\frac{1}{2}}(x)$, $K_{n+\frac{1}{2}}(x)$ n a positive integer and x any real number greater than 0. Starting with the integral representation of $I_{n+\frac{1}{2}}(x)$ [8]

$$I_{n+\frac{1}{2}}(x) = \frac{x^{n+\frac{1}{2}}}{\sqrt{\pi}\, 2^{n+1/2} n!} \int_{-1}^{1} e^{-xt}(1-t^2)^n dt,$$

clearly

$$\frac{x^{n+\frac{1}{2}} e^{-x}}{\sqrt{\pi}\, 2^{n+1/2} n!} \int_{-1}^{1} (1-t^2)^n dt \leq I_{n+\frac{1}{2}}(x)$$

$$\leq \frac{x^{n+\frac{1}{2}} e^{x}}{\sqrt{\pi}\, 2^{n+1/2} n!} \int_{-1}^{1} (1-t^2)^n dt.$$

To evaluate $\int_{-1}^{1} (1-t^2)^n dt$ we write the integral as $\int_{-1}^{1} (1+t)^n (1-t)^n dt$ and, by repeated integration by parts, we obtain

$$\int_{-1}^{1} (1-t^2)^n dt = \frac{(n!)^2 2^{2n+1}}{(2n+1)!} .$$

Hence

$$\frac{(2x)^{n+\frac{1}{2}} e^{-x} n!}{\sqrt{\pi}\,(2n+1)!} \leq I_{n+\frac{1}{2}}(x) \leq \frac{(2x)^{n+\frac{1}{2}} e^{x} n!}{\sqrt{\pi}\,(2n+1)!} .$$

Taking the integral representation of $K_{n+\frac{1}{2}}(x)$ [8]

$$K_{n+\frac{1}{2}}(x) = \frac{\sqrt{\pi}\, x^{n+\frac{1}{2}}}{n!\, 2^{n+1/2}} \int_{1}^{\infty} e^{-xt}(t^2-1)^n \, dt$$

we set u+1 = t and obtain

$$\int_1^{\infty} e^{-xt}(t^2-1)^n dt = e^{-x}\int_0^{\infty} e^{-xu}(u^2+2u)du$$

$$\geq e^{-x}\int_0^{\infty} e^{-x}\, u^{2n}du = \frac{(2n)!}{x^{2n+1}}\, e^{-x}.$$

On the other hand

$$\int_1^{\infty} e^{-xt}(t^2-1)^n dt \leq \int_1^{\infty} e^{-xt}t^{2n}dt \leq \int_0^{\infty} e^{-xt}t^{2n}dt = \frac{(2n)!}{x^{2n+1}} ;$$

so we have

$$\frac{e^{-x}(2n)!\sqrt{\pi}}{(2x)^{n+1/2}n!} \leq K_{n+\frac{1}{2}}(x) \leq \frac{(2n)!\sqrt{\pi}}{(2x)^{n+1/2}n!} .$$

Taking the definition of $\gamma_n(k,x,\rho)$, $\rho > 0$, $k > 0$ (Appendix (2)) we can easily derive:

$$\frac{e^{-k(x+\rho)}}{2n+1}\left(\frac{x}{\rho}\right)^{n+\frac{1}{2}} \leq \gamma_n(k,x,\rho) \leq \frac{e^{kx}}{2n+1}\left(\frac{x}{\rho}\right)^{n+\frac{1}{2}} \quad \text{for } 0 \leq x \leq \rho$$

$$\frac{e^{-k(x+\rho)}}{2n+1}\left(\frac{\rho}{x}\right)^{n+\frac{1}{2}} \leq \gamma_n(k,x,\rho) \leq \frac{e^{k\rho}}{2n+1}\left(\frac{\rho}{x}\right)^{n+\frac{1}{2}} \quad \text{for } x > \rho.$$

In the series of integrals of Sections 3,4,5 and 6 we replace the γ's by these majorant and minorant functions to obtain majorant and minorant series of integrals. We then can find lower and upper bounds for the terms of these minorant and majorant series, respectively, by the following inequalities:

$$\frac{e^{-kx}x^{n+1}}{n+1} \leq \int_0^x e^{-ky}y^n dy \leq \frac{x^{n+1}}{n+1}$$

$$\frac{x^{n+1}}{n+1} \leq \int_0^x e^{ky}y^n dy \leq \frac{e^{kx}x^{n+1}}{n+1}$$

$$\int_x^\infty e^{-ky}y^n dy \leq \frac{e^{-kx}}{(n-1)x^{n-1}}$$

n a positive integer greater than 1, and x,k real numbers greater than 0.

We shall also use the following definitions in this paper:

$$\left\{\begin{array}{lll} x_+ = x; & & x \geq 0 \\ x_+ = 0; & & x < 0 \end{array}\right\}$$

$$\left\{\begin{array}{lll} x_- = x; & & x \leq 0 \\ x_- = 0; & & x > 0 \end{array}\right\} \quad .$$

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